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(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 581 550 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **93305859.6**

(51) Int. Cl.[5] : **C01B 11/02**

(22) Date of filing : **23.07.93**

(30) Priority : **23.07.92 IL 102627**

(43) Date of publication of application :
02.02.94 Bulletin 94/05

(84) Designated Contracting States :
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE

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(54) Solid compositions capable of releasing chlorine dioxide.

(57) A solid composition capable of releasing chlorine dioxide in water comprises (a) a water soluble chlorite salt, (b) an oxidizing chlorine-releasing agent in the form of sodium- and/or potassium-dichloro-s-triazinetrione(s) and/or trichloro-s-triazinetrione(s), and (c) a proton-donor serving as a water soluble agent capable of lowering the pH of an aqueous solution to less than 3. The chlorite salt (a) is advantageously a sodium or potassium salt. The proton-donor is advantageously sodium- and/or potassium-hydrogen sulphate(s) and/or pyrosulphate(s), or alternatively citric acid and/or malic acid. The stoichiomolecular ratio of the various components in the composition should be chlorite salt : oxidizing chlorine-releasing agent : proton-donor = 4 : 1 : 3, but a slight excess of the proton-donor may be advantageous. The solid compositions may safely be manufactured, stored and transported.

Aqueous solutions in which the solid composition has been dissolved release chlorine dioxide quite quickly and almost quantitatively, and find use wherever chlorine dioxide is employed in industrial and water-treatment installations and processes. The solid compositions are also useful in antiseptic and sanitizing preparations.

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The present invention relates to solid compositions capable of releasing chlorine dioxide very quickly on dissolution in water.

Chlorine dioxide (ClO_2) is an oxychlorine compound which is gaseous at room temperature and normal pressure, and it is of course well-known and widely used for a number of applications.

Thus in its capacity as an oxidizing agent it is well-accepted for bleaching pulp in the paper industry, for bleaching fabrics, for the oxidative deodorization of malodorous substances in water and waste water, and indeed for some other industrial uses. Moreover, in its capacity as a source of chlorine it can advantageously by used as a biocide and sanitizer, replacing chlorine itself in the treatment of potable water and more generally as a disinfectant or antiseptic.

The even more widespread use of chlorine dioxide is however restricted by two factors:

1. Chlorine dioxide cannot be stored and transported as a gas, while its solubility in water is limited, and the solution is unstable; while anyway
2. Chlorine dioxide as a gas is very toxic, with a specific effect on the respiratory tract.

In view of the difficulties involved in the preparation of chlorine dioxide and the dangers attached in its storage and transportation, on the whole its use is therefore confined to installations where the production of ClO_2 can take place "on-site", thus located near the point-of-use.

The known manufacturing processes for chlorine dioxide are based on one or other of two source substances, namely either sodium chlorite or sodium chlorate. In all the known processes it is necessary to add a second reactant in great excess to one or other of the above-mentioned source substances, in order thereby to displace the reaction equilibrium to such a degree as to achieve the maximum yield of chlorine dioxide in a minimum of time. Thus for instance in one particular process the addition of an excess of lactic acid (which is an organic acid) to a solution of sodium chlorite ($NaClO_2$) shifts the equilibrium between chlorine dioxide and chlorous acid in that solution and leads to the evolution of chlorine dioxide, but the yield of the latter is always far short of 100%.

Against the background outlined above, clearly there is a great and long-standing need for a solid composition which would be safe to manufacture, store, transport and use, and yet be capable of very quickly releasing chlorine dioxide upon dissolution in water, with a yield approaching 100%, utilizing only a minimal excess of reagents and equally yielding only minimal amounts of by-products, e.g. chlorine, chlorous acid, chloric acid, etc.

According to the present invention there is provided a solid composition comprising:

(a) a chlorite salt;

(b) an oxidizing chlorine- releasing agent in the form of one or more solium- and/or potassium- dichloro-s-triazinetrione(s) and/or -trichloro-s-triazinetrione(s); and,

(c) a proton-donor serving as a water-soluble agent capable of lowering the pH of the aqueous solution to less than 3.

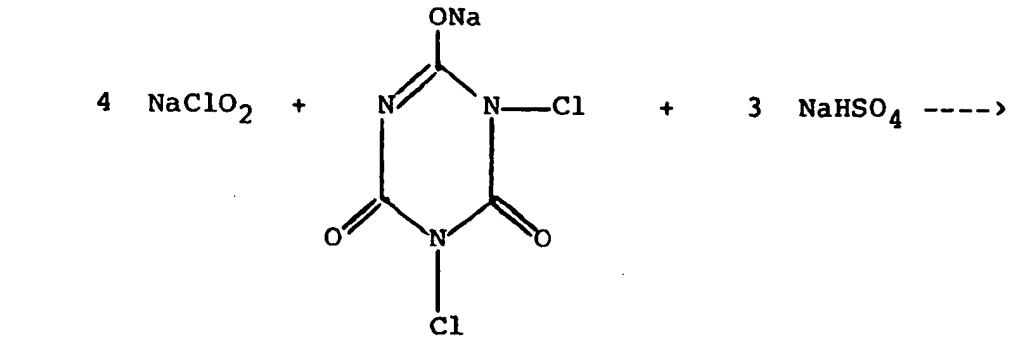
There are a number of known oxidizing chlorine-releasing salts which are capable of use in the compositions of this invention, including for instance trichloro isocyanurate, but in our experience the most effective such compound, which therefore is preferred, is dichloro isocyanurate (Na-DCC).

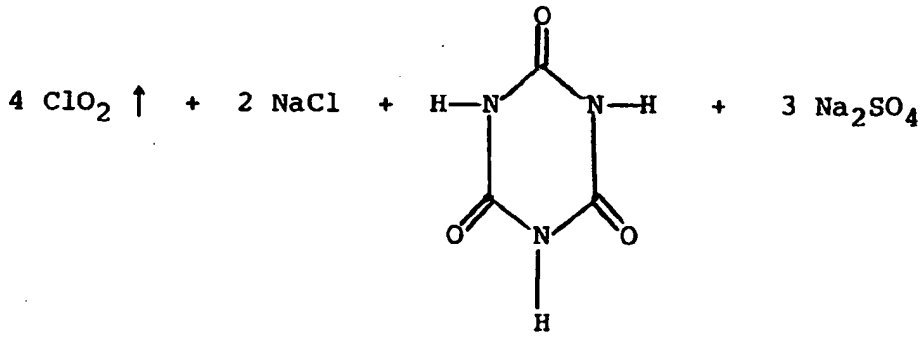
Suitable proton-donors include, for example, a variety of inorganic acid salts, such as sodium- or potassiumhydrogen sulphates or pyrosulphates, as well as certain organic acids, e.g. citric acid, malic acid, (racemate or optical antipode), etc.

The various specified components namely chlorite salt (a), oxidising chlorine-releasting agent (b) and proton-donor (c) in the composition of this invention will preferably be present in substantially the following molar ratios:

$$(a) : (b) : (c) = 4 : 1 : 3$$

so that the reaction proceeds in accordance with the following chemical equation:





The proton-donor $NaHSO_4$ may of course be present in a small excess.

The invention includes a process for the preparation of the composition according to the present invention, in which the above-specified dry components are brought together and thoroughly admixed under substantially anhydrous conditions.

It also extends to a chlorine-dioxide-containing aqueous solution formed by dissolving the solid composition in water. On being dissolved in a suitable amount of water the composition according to the present invention evolves chlorine dioxide in a yield approaching 100%. Moreoer, the release of chlorine dioxide is surprisingly fast, and the equilibrium of the reaction shown above is thereby irreversibly displaced to the right, yielding the desired product in more or less the strict stoichiomolecular ratio. Furthermore, while of course we cannot rule out all possibility that the reaction might sometimes give rise to the kind of by-products obtained in similar reactions (e.g. chlorine, chlorous acid and chloric acid) in our experience that does not happen, at least within the limits of our analytical determinations.

According to another aspect of the present invention there is also provided a process for the production of chlorine dioxide in which a composition as herein disclosed is dissolved in a suitable amount of water.

As already indicated above chlorine dioxide in aqueous solution is well-known to be an excellent biocide, virucide, bactericide, fungicide, algaecide and sporocide. It is able to exert its effect on such microorganisms after only a short period of contact, usually a matter of merely minutes. The presence of proteins or other contaminating substances does not inhibit its effect on the microorganisms. The use of chlorine dioxide in aqueous solution also seems to be free from any danger of an halogenation reaction occurring.

Thus the composition and the process according to the present invention provide means for releasing chlorine dioxide immediately, easily and safely, under controlled conditions. As the reaction is fast and nearly complete, the toxic side-effects of any residual by-products are restricted to a minimum - and this enables the use of the composition as an antiseptic for skin, mucous membranes and even in body cavities.

In yet another aspect of this invention there are provided antiseptic and sanitizing preparations containing the solid composition and/or aqueous solution thereof, optionally together with other usual additives.

For similar reasons, the compositions of this invention are suitable for use in th treatment of potable water, e.g. as a swimming pool sanitizer and for other water and waste-water treatm nts.

The amount of water in which the composition can effectively be dissolved can vary very widely, dependent on the kind of use envisaged - and indeed there can be situations in which the humidity of the ambient air may be sufficient to release chlorine dioxide from the solid composition.

In order that the present invention shall be well understood it will be described in more detail, but only by way of illustration, with reference to the following Examples (and Comparative Examples), in which abbreviation

"T.G." is used to mean "technical grade", while the abbreviation "C.P." is used to mean "chemically pure".

EXAMPLE 1

A solid composition in accordance with the invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G 80%)	42 g.
Na-DCC (T.G. 96%)	22 g.
Sodium Bisulfate (C.P)	36 g.
	100 g.

1 Gram of this solid composition was then dissolved in 99 grams of water, yielding a yellowish-green solution containing approximately 0.25% of chlorine dioxide. This corresponds to a yield of approximately 100%, based on the sodium chlorite.

EXAMPLE 2

A solid composition in accordance with the invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	42 g.
Na-DCC (T.G. 96%)	22 g.
Sodium Pyrosulphate (C.P.)	36 g.
	100 g.

1 Gram of this solid composition was dissolved in 99 grams of water, yielding a yellowish-green solution containing approximately 0.25% of chlorine dioxide. This corresponds to a yield of approximately 100% based on the sodium chlorite.

EXAMPLE 3

A solid composition in accordance with the invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	40.3 g.
Na-DCC (T.G. 96%)	20.7 g.
Potassium Bisulphate (C.P)	39.0 g.
	100.0 g.

1 Gram of this solid composition was dissolved in 99 grams of water, yielding a yellowish-green solution containing approximately 0.24% of chlorine dioxide. This corresponds to a yield of approximately 100% based on the sodium chlorite.

EXAMPLE 4

A solid composition in accordance with the invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	40.3 g.
Na-DCC (T.G. 96%)	20.7 g.
Potassium Pyrosulphate (C.P.)	39.0 g.
	100.0 g.

1 Gram of this solid composition was dissolved in 99 grams of water, yielding a yellowish-green solution containing approximately 0.24% chlorine dioxide. This corresponds to a yield of approximately 100% based on the sodium chlorite.

EXAMPLE 5 (Comparative)

Merely for purposes of comparison (especially with Examples 6 and 7 below) a solid composition free from Na-DCC (or any other oxidizing chlorine-releasing salt) and therefore outside the scope of this invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	42.5 g.
Sodium Bisulphate (C.P.)	50.0 g.
Sodium Chloride (C.P.)	7.5 g.
	100.0 g.

This composition was dissolved in water, whereupon the evolution of chlorine dioxide started and then continued slowly for a few days. Immediately following dissolution the yield of chlorine dioxide was found to be 78%; after 30 minutes the yield had increased to 30%; and at the end of 3 days the final yield obtained had reached 63%.

EXAMPLE 6 (Comparative)

Again for purposes of comparison (especially with Example 5 above and Example 7 below) a solid composition free from any proton-donor and therefore outside the scope of this invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	49.0 g.
Na-DCC (T.G. 96%)	51.0 g.
	100.0 g.

This composition was dissolved in water, and thereupon a very slow release of chlorine dioxide could be detected - but initially it measured only 1%, and after 30 minutes it was still only 5%, while even after 3 hours it had attained no more than 30%. Some release of oxygen was also observed.

EXAMPLE 7

A solid composition in accordance with this invention (although a somewhat less-preferred one, containing trichloroisocyanurate instead of Na-DCC), was prepared (especially for purposes of contrast with Comparative Examples 5 and 6 above) by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	42.0 g.
Trichloroisocyanurate (C.P.)	15.0 g.
Sodium Bisulphate (C.P.)	43.0 g.
	100.0 g.

This composition was dissolved in water. As compared with the more-preferred compositions of Example 1 - 4, it was clear that the replacement of Na-DCC by trichloroisocyanurate slowed down the rate of release of the chlorine dioxide - but, even so, it was found that the release of chlorine dioxid had attained about 100% within 10-15 minutes.

EXAMPLE 8

A solid composition in accordance with this invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	42 g.
Na-DCC (T.G. 96%)	22 g.
Citric Acid (C.P.)	36 g.
	100 g.

1 Gram of this solid composition was dissolved in 99 grams of water, yielding a yellowish-green solution containing approximately 0.25% chlorine dioxide. This corresponds to a yield of approximately 100% based on the sodium chlorite.

EXAMPLE 9

A solid composition in accordance with this invention was prepared by intimately mixing together the following ingredients in the following amounts:

Sodium Chlorite (T.G. 80%)	42 g.
Na-DCC (T.G. 96%)	22 g.
D.L-Malic Acid (C.P.)	36 g.
	100 g.

1 Gram of this solid composition was dissolved in 99 grams of water, yielding a yellowish-green solution containing approximately 0.25% chlorine dioxide. This corresponds to a yield of approximately 100% based on the sodium chlorite.

Claims

1. A solid composition capable of releasing chlorine dioxide upon dissolution in water, said composition comprising:
   (a) a water-soluble chlorite salt;
   (b) an oxidizing chlorine-releasing agent, in the form of one or more sodium- and/or potassium- dichloro-s-triazinetrione(s)s and/or trichloro- s-triazinetrione(s) ; and
   (c) a proton-donor serving as a water-soluble agent capable of lowering the pH of an aqueous solution to less than 3.

2. A solid composition as claimed in claim 1, in which the chlorite salt (a) is or includes the sodium- and/or potassium salt(s) thereof.

3. A solid composition as claimed in claim 1 or claim 2, in which the proton-donor (c) is or includes one or more sodium- and/or potassium- hydrogen sulphate(s) and/or pyrosulphate(s).

4. A solid composition as claimed in claim 1 or claim 2, in which the proton-donor is or includes citric acid and/or malic acid.

5. A solid composition as claimed any of the preceding claims, in which the stoichiomolecular ratio of com-

ponents (a) : (b) : (c) is substantially 4 : 1 : 3.

6. A solid composition as claimed in claim 5, in which the prot in-donor (c) is present in a slight stoichiomol cular excess relative to the other components.

7. A chlorine-dioxide-containing aqueous solution formed by dissolving a solid composition as claimed in any of the preceding claims in water.

8. A solution as claimed in claim 7, in which the composition has been dissolved in a concentration of the order of 1% by weight.

9. Antiseptic and sanitizing preparations containing as biocidally-active ingredient therein a solid composition and/or an aqueous solution as claimed in any of the preceding claims optionally together with other usual additives appropriate to their function.

10. In an industrial and/or water-treatment process utilizing chlorine dioxide the step of generating said chlorine dioxide by dissolving a solid composition as claimed in any of claims 1 to 6 in water extemporaneously in situ within the processing installation.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 5859

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-2 712 574 (MINNESOTA MINING AND MANUFACTURING CO) * claims 1-15 *	1	C01B11/02
A	US-A-4 547 381 (MASON ET AL) * examples 1-6 *	1	
A	DATABASE WPI Week 8847, Derwent Publications Ltd., London, GB; AN 88-333818 & JP-A-63 246 304 (HELTH KOSAN KK) * abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	25 OCTOBER 1993	CLEMENT J-P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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